



HAL
open science

Lipidic polyols using Thiol-ene/yne strategy for crosslinked Polyurethanes

Phuoc Dien Pham, Vincent Lapinte, Yann Raoul, Jean Jacques Robin

► To cite this version:

Phuoc Dien Pham, Vincent Lapinte, Yann Raoul, Jean Jacques Robin. Lipidic polyols using Thiol-ene/yne strategy for crosslinked Polyurethanes. *Journal of polymer science: Part A, General papers*, 2014, pp.1597-1606. 10.1002/pola.27159 . hal-01072015

HAL Id: hal-01072015

<https://hal.science/hal-01072015>

Submitted on 7 Oct 2014

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Lipidic polyols using Thiol-ene/yne strategy for crosslinked Polyurethanes

Pham P. D.,^a Lapinte V.,^{a*} Raoul Y.,^b Robin J.-J.^a

^a: Institut Charles Gerhardt Montpellier UMR5253 CNRS-UM2-ENSCM-UM1 - Equipe Ingénierie et Architectures Macromoléculaires, Université Montpellier II – Bat 17 – cc1702, Place Eugène Bataillon 34095 Montpellier Cedex 5.

^b: Société Interoléagineuse d'Assistance et de développement (S.I.A.), 11, rue de Monceau CS 60003 75378 Paris cedex 08, France.

Phuoc-Dien.Pham@univ-montp2.fr,

Vincent.Lapinte@univ-montp2.fr, y.raoul@novance.com, Jean-Jacques.Robin@univ-montp2.fr

RECEIVED DATE (to be automatically inserted after your manuscript is accepted if required according to the journal that you are submitting your paper to)

TITLE RUNNING HEAD. Lipidic polyols for polyurethane materials.

CORRESPONDING AUTHOR FOOTNOTE. Institut Charles Gerhardt Montpellier UMR5253 CNRS-UM2-ENSCM-UM1, Equipe Ingénierie et Architectures Macromoléculaires, Université Montpellier II cc1702, Place Eugène Bataillon. 34095 Montpellier Cedex 5, France. Tel: 33-4-67-14-48-32; fax: 33-4-67-14-40-28. Vincent.Lapinte@univ-montp2.fr

Abstract

Oleic acid and diacid were converted into propargylic esters followed by thiol-ene/yne coupling (TEC/TYC) functionalization in presence of mercaptoethanol. The multi-radical addition on fatty esters leads to the formation of lipidic polyols (OH1 and OH2), as judged by ^1H NMR and mass spectroscopies as well as by steric exclusion chromatography (SEC). The crosslinking reaction between TEC/TYC-based polyols and MDI isocyanate reactant was monitored by FTIR experiment and reaction parameters were optimized. By differential scanning calorimetry (DSC), relatively high glass transitions are measured corresponding to structure with little or without dangling chain. Moreover, the thermal stability of the resulting plant oil-based polyurethane materials (PU1 and PU2) were found to be fully consistent with that of other lipidic polyurethanes respecting a three-step process. Thanks to TYC methodology, fatty diacid produces lipidic polyol without dangling chain and lipidic thermoset PU with relatively high Tg.

Keywords: fatty acid; polyol; polyurethane; thiol-yne coupling.

Introduction

With growing concerns over sustainable development and environmental impact of petrochemical polymer products, researchers are paying more attention to bio-based materials. The main bio-based materials are vegetable oils, polysaccharides, sugars and woods¹ that are chemically modified for the development of chemicals, plasticizers,² polymers,³ blends,⁴ composites, and coatings.⁵ In particular, vegetable oils and their derivatives (fatty alcohols, esters and acids) have been extensively modified to generate bio-based materials⁶ such as polyamides,⁷ non-isocyanate polyurethanes,^{8,9} surfactants,¹⁰ and epoxy resins.¹¹⁻¹³

Polyurethanes (PU) are very interesting polymeric materials allowing a huge variety of industrial applications from paints, coatings, adhesives, sealants and insulation foams. They are synthesized from polyol and poly(isocyanate) reactants producing carbamate (urethane) bonds. The conversion of unsaturated oils into polyols has been widely investigated to prepare polyurethanes with different physical and chemical properties. There are several approaches to introduce the hydroxyl group into the vegetable oils structure. To date, the synthesis of lipidic polyol has been mainly accomplished from epoxy vegetable oils or fatty ester intermediate (Table 1). The ring-opening of oxirane by various nucleophiles like alcohol (methanol,¹⁴ propylene glycol¹⁵) or carboxylic acid (lactic acid¹⁶) was described. An alternative approach consists in the oligomerization of fatty ester by ring-opening of epoxy groups in presence of catalyst based on aluminum.¹⁷ Ozonolysis of oils and further reduction of terminal acid groups also lead to lipidic polyols.¹⁸ Cadiz *et al.* explored another strategy by hydrosilylation of methyl 10-undecenoate with phenyl tris(dimethylsiloxy)silane (PTDS).¹⁹ Additionally, polyols were prepared by radical pathway: thiol-ene coupling (TEC) using mercaptoethanol in presence of raw oil²⁰ or fatty esters.^{21,22} One drawback of plant oil-based PU is the low T_g value (<40°C) due to both the low functionality of polyols and the presence of dangling

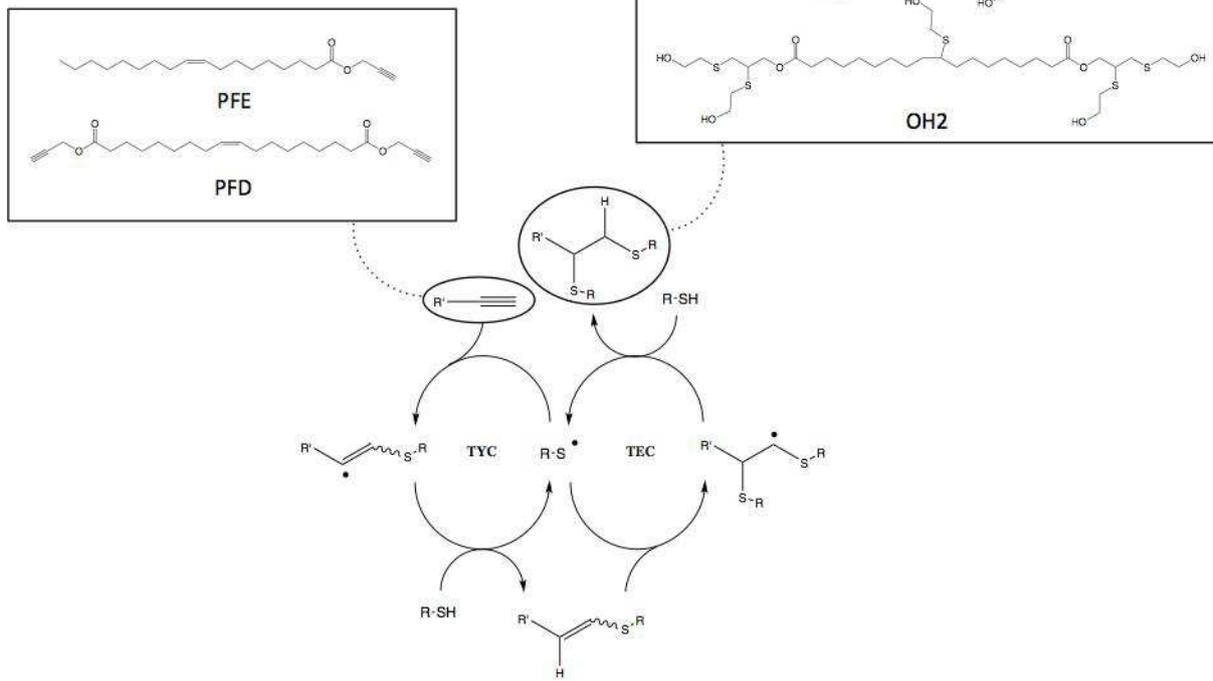
chains which act as plasticizers.

Table 1. Comparison of polyols synthesized in this work and in the literature.

Reference	Lipidic precursor	Structure	Strategy	Reactant
(1)	various VO	FA	ROEG and esterification	propylene glycol
(2)	soybean	TAG	ROEG	lactic acid
(3)	various VO	TAG	ROEG	methanol
(4)	methyloleate	oligomer	ROEG and reduction	LiAlH ₄
(5)	various VO	TAG	ozonolysis and reduction	O ₃ and NaBH ₄
(6)	methyloleate	TAG	hydrosilylation and reduction	PTDS and AlLiH ₄
(7)	rapeseed oil	TAG	TEC	HS-(CH ₂) ₂ OH
(8)	methyloleate	FA	allylation + TEC	HS-(CH ₂) ₂ OH
(9)	methyloleate	FA	dehydrobromation + TYC	HS-(CH ₂) ₂ OH
OH1	oleate acid	FA	esterification + TYC	HS-(CH ₂) ₂ OH
OH2	oleatediacid	FA	esterification + TYC	HS-(CH ₂) ₂ OH

TAG: triacyl glycerol; FA: fatty acid; VO: vegetable oil; ROEG: ring-opening epoxy group; PTDS: phenyl tris(dimethylsiloxy)silane.

Herein, we report a new synthetic approach for the facile synthesis of lipidic polyols *via* thiol-ene/yne coupling (TEC/TYC) using 2-mercaptoethanol (Scheme 1).²³ The TYC splits in two cycle mechanism.²⁴ In the first cycle, the thiyl radicals generated from thiol groups were added on the ethynyl groups to form a vinyl sulfide radical, which could attract a hydrogen atom from a thiol group, producing the vinyl sulfide and generating another thiyl radical at the same time. In the second cycle, a thiyl radical adds on the double bond of the vinyl sulfide, generating a dithioether radical, which attracts a hydrogen atom from a thiol groups and forms the disubstituted product. This synthetic strategy leads to high-functional polyols since one ethynyl group turns into two thioether groups. By this methodology, propargylic fatty acid (PFE) and diacid (PFD) were converted into lipidic polyols (OH1) and (OH2), respectively. Cadiz *et al.* have already synthesized lipidic polyols by thiol-yne coupling after bromination, dehydrobromination of 10-undecenoic and 9-octadecenoic acids.^{25,26} However the ethynyl group is in internal position, along the fatty chain whereas in our case it is in terminal position *via* propargylic precursor. The advantage of our strategy is to obtain, in the case of diacid, a polyol without dangling chain and plant oil-based PUs with relatively high Tg value. The polyols were carefully characterized by NMR and mass spectroscopies as well as size exclusion chromatography. Finally, crosslinked polyurethanes from lipidic polyols (OH1 and OH2) and MDI isocyanate reactant were investigated in terms of thermal properties and stability by DSC and TGA techniques.



Scheme 1

Experimental part

Materials

Triethylamine, 2-mercaptoethanol, thionyl chloride, propargylic alcohol, 2,2-dimethoxy-2-phenylacetophenone (DMPA), oleic chloride and 4,4'-methylenebis(phenylisocyanate) (MDI) were purchased from Aldrich and were used as received. *N,N*-dimethylformamide (DMF) and chloroform were dried and distilled according to standard procedures. Oleic diacid was generously gifted by S.I.A.. Deuterated solvents were purchased from SDS and were used without further purification. 2,2'-Azobisisobutyronitrile (AIBN) was purified twice by recrystallization in methanol and dried under vacuum. Commercially available reagents and solvents were purified and dried, when necessary, by standard methods prior to use.

Analytical Techniques

^1H and ^{13}C NMR spectra were recorded using a Bruker AC 300 and 400 MHz with CDCl_3 as solvent. Chemical shifts (^1H NMR) were referenced to the peak of residual CHCl_3 at 7.26 ppm. Chemical shifts (^{13}C NMR) were referenced to CDCl_3 at 77 ppm. Fourier Transform Infrared (FTIR) spectra were recorded with a Perkin–Elmer Spectrum 100 spectrometer equipped with an attenuated total reflectance (ATR) crystal made of ZnSe. Size exclusion chromatography (SEC) analyses were performed in DMAc (0.1% LiCl) as eluent. Two PL-gel mix C columns were used at 50 °C with a flow rate of 0.8 mL.min⁻¹, calibrated using PS standards. Differential scanning calorimetry (DSC) analyses of the samples were carried out on 5-10 mg samples in aluminum pans, using a Mettler Toledo apparatus. The DSC heating and cooling schedules used were as follows: the samples were heated at 10 °C.min⁻¹ and cooled at the same rate to room temperature. LC/ESI-MS chromatograms were acquired in the positive ion mode with the capillary voltage set at 3000 V and cone voltage at 30 V while the

dry temperature was set at 350 °C and dry gas flow was maintained at 13 mL.min⁻¹. The mass acquisition range was from m/z 50 to 1000. The thermo-oxidative stability of the polyurethane materials was examined using a Q50 thermogravimetric analyzer (TGA) from TA Instruments[®]. The experiments consisted in registering the weight loss of the sample under nitrogen flow (60 mL.min⁻¹) as a function of temperature from the ambient up to 550 °C. Different experiments were heated at 10 °C.min⁻¹.

Conversion of oleic diacid into fatty diacid chloride(DCI)

In a 500 mL two-necked flask equipped with a reflux condenser and a dropping funnel, 53.5 g (171.2 mmol) of oleic diacid were dissolved in 150 mL of dry chloroform. The chloroform solution (200 mL) containing thionyl chloride was added dropwise over a period of 1 h. The mixture was heated gently on an oil bath held at 60 °C for 16 hours. The mixture was evaporated under pressure in order to remove any excess of thionyl chloride. The product was used without any further purification in 97% yield.

¹H NMR (CDCl₃, 300 MHz) δ (ppm): 1.16–1.48 (16H, H₄₋₇, H₁₂₋₁₅), 1.55–1.82 (4H, H₃, H₁₆), 1.86–2.12 (4H, H₈, H₁₁), 2.79–2.98 (4H, H₂, H₁₇), 5.25–5.41 (2H, H₉, H₁₀).

Synthesis of propargylic esters

Propargylic alcohol (7.71 g, 137.4 mmol) and triethylamine (13.9 g, 137.4 mmol) were dissolved in dry dichloromethane (100 mL). The solution was cooled in an ice bath under N₂ for 15 min. At 0 °C, dichloromethane solution (100 mL) of diacid chloride (20 g, 57.2 mmol) was added dropwise to the previous solution over 1 h. The stirring was continued for one additional hour. Then, the mixture refluxed for 16 h. The solution was washed with water (3x 200 mL) and brine (2x 100 mL), dried over anhydrous MgSO₄, filtered, and evaporated under reduced pressure to yield a brown oil (19.2 g, 86 %).

Propargylic fatty ester (PFE)

^1H NMR (CDCl_3 , 300 MHz) δ (ppm): 0.79–0.95 (3H, H_1), 1.15–1.44 (20H, H_{2-7} , H_{12-15}), 1.52–1.72 (2H, H_{16}), 1.87–2.11 (4H, H_8 , H_{11}), 2.27–2.39 (2H, H_{17}), 2.45–2.50 (2H, H_{21}), 4.60–4.72 (4H, H_{19}), 5.26–5.41 (2H, H_9 , H_{10}). 23.35 g, 81% yield.

^{13}C NMR (CDCl_3 , 100 MHz) δ (ppm): 14.04 (C_1), 22.64 (C_2), 24.74 (C_{16}), 27.10 and 27.16 (C_8 , C_{11}), 28.99–29.72 (C_{4-7} , C_{12-15}), 31.87 (C_3), 33.88 (C_{17}), 51.63 (C_{19}), 74.61 (C_{21}), 77.74 (C_{20}), 129.62 and 129.89 (C_9 , C_{10}), 172.72 (C_{18}).

FTIR (cm^{-1}): 3312 (O-H), 2923 and 2853 (C-H_{stretching}), 1744 (C=O_{ester stretching}).

Propargylic fatty diester (PFD)

^1H NMR (CDCl_3 , 300 MHz) δ (ppm): 1.17–1.41 (16H, H_{4-7} , H_{12-15}), 1.61–1.71 (4H, H_3 , H_{16}), 1.88–2.08 (4H, H_8 , H_{11}), 2.24–2.40 (4H, H_2 , H_{17}), 2.45–2.49 (2H, H_{21}), 4.60–4.70 (4H, H_{19}), 5.26–5.38 (2H, H_9 , H_{10}). 19.2 g, 86 % yield.

^{13}C NMR (CDCl_3 , 100 MHz) δ (ppm): 24.27 ($\text{C}_3, \text{C}_{16}$), 26.10 (C_8 , C_{11}), 27.97, 28.01, 28.08 (C_{4-7} , C_{12-15}), 32.80 (C_2 , C_{17}), 50.61 (C_{19}), 73.86 (C_{21}), 76.85 (C_{20}), 128.73 (C_9 , C_{10}), 171.51 (C_1 , C_{18}).

FTIR (cm^{-1}): 3294 (O-H), 2926 and 2854 (C-H_{stretching}), 1739 (C=O_{ester stretching}).

Thiol-en/yne coupling (TEC/TYC) between mercaptoethanol and propargylic fatty esters

In a 50 mL flask, PFD (5 g, 12.86 mmol) was reacted with 2-mercaptoethanol (15.07 g, 193 mmol) in presence of the radical initiator DMPA (1.65 g, 6.43 mmol) under N_2 atmosphere. An amount of DMF (2.4 mL) was added to dissolve the photoinitiator. The reaction carried out under UV irradiation (365 nm) at room temperature for 8 h. DMF was then removed under reduced pressure. The mixture was dissolved in CHCl_3 (200 mL), then

washed with water (3x200 mL), and brine (2x200 mL), dried over anhydrous MgSO₄, filtered, and evaporated under reduced pressure to yield a dark yellow oil. The product was purified by column chromatography using AcOEt/CH₂Cl₂ 3/7, as eluent, to afford a viscous light yellow product (6.59 g, 66%).

Polyol derivating from PFE (OH1)

¹H NMR (CDCl₃, 400 MHz) □ (ppm): 0.81-1.02 (3H, H₁), 1.15–1.76 (29H, H₂₋₁₆), 2.27–2.44 (2H, H₁₇), 2.53–3.23 (11H, H₂₀, H₂₁, H₂₂, H₂₄), 3.63–3.91 (6H, H₂₃, H₂₅), 4.06–4.43 (2H, H₁₉).

¹³C NMR (CDCl₃, 100 MHz) □ (ppm): 13.52 (C₁), 22.05 (C₂), 24.23 (C₁₆), 26.02–29.01 (C₄₋₈, C₁₂₋₁₅), 31.25 (C₃), 32.77 (C₁₇), 33.56–35.27 (C₉, C₁₁, C₂₁, C₂₂), 44.43 (C₁₀), 45.32 (C₂₀), 60.54, 60.86 (C₁₉, 2 x C₂₃), 64.77 (C₂₅), 173.15 (C₁₈).

FTIR (cm⁻¹): 3389 (O-H), 2930 and 2858 (C-H_{stretching}), 1736 (C=O_{ester stretching}).

Polyol derivating from PFD (OH2)

¹H NMR (CDCl₃, 400 MHz) δ (ppm): 1.14-1.65 (27H, H₂₋₁₆), 2.21-2.36 (4H, H₂, H₁₇), 2.64–2.93 (18H, H₂₁, H₂₂, H₂₄), 2.99–3.16 (2H, H₂₀), 3.43 (OH), 3.61–3.80 (10H, H₂₃, H₂₅), 4.13–4.39 (4H, H₁₉).

¹³C NMR (CDCl₃, 100 MHz) δ (ppm): 24.27 (C₃, C₁₆), 26.06–28.88 (C₄₋₈, C₁₂₋₁₅), 32.86 (C₂, C₁₇), 33.61, 34.36, 35.41, 32.77 (C₉, C₁₁, C₂₁, C₂₂), 44.51 (C₁₀), 45.33 (C₂₀), 60.50, 60.84 (C₁₉, 4 x C₂₃), 64.84 (C₂₅), 173.20 (C₁, C₁₈).

ESI-MS (m/z): [M+H]⁺theo: 779.33 and found: 779.40, [M-(C₇H₁₅O₃S₂)]⁺theo: 567.30 and found: 567.3.

FTIR (cm⁻¹): 3375 (OH), 2931 and 2856 (C-H_{stretching}), 1731 (C=O_{ester stretching}).

General procedure for crosslinked polyurethanes (PU1 and PU2)

The PU materials were prepared by mixing OH1 or OH2 with 4,4'-methylenebis(phenyl isocyanate) (MDI) at 60 °C in an aluminum mold. The [NCO]/[OH] ratio ranged from 1/1 to 1.1/1. The vacuum was applied to remove bubbles. The mixture was cured at 60 °C for 24h and post-cured at 110 °C for 24h. The resulting PU materials were peeled off from the mold for characterization tests.

Results and discussion

The various approaches described in the literature to synthesize lipidic polyols are summarized in Table 1. Herein, we focus the discussion on the lipidic polyols used in thermoset polyurethanes in presence of MDI isocyanate. Three lipidic structures are mentioned: i) the triacylglycerols (TAG) (**2**, **3**, **5** and **7**), ii) the linear fatty acid derivatives (FA) (**1**, **8** and **9**), and iii) other structures like three-arm stars (**6**) and oligomers (**4**). It is interesting to note that the presence of dangling chain was observed in almost all structures, except for **5** and **6**. Otherwise, some structures carry primary alcohol groups (**1**, **5**, **6**, **7**, **8** and **9**) while others carry secondary ones (**2**, **3** and **4**). This comparative study also highlights the presence of ester group in polyol structures apart from **4**, **6**, **8** and **9**. Herein, we proposed two types of polyol based on oleic acid and diacid. From the first one, a triol (OH1) bearing an ester group and a dangling chain was elaborated whereas a pentaol (OH2) bearing a diester structure without dangling chain was synthesized using fatty diacid.

Synthesis of propargylic fatty ester and diester

The synthesis of propargylic fatty ester (PFE) and diester (PFD) starts from activated species of oleic (di)acids. The oleic chloride (OACl) is marketed whereas the corresponding diacid (DCI) is easily synthesized in 97% yield (see experimental part). Thus, the treatment of OACl and DCI with propargylic alcohol in presence of triethylamine in CH₂Cl₂ afforded PFE and PFD in a good yield (81 and 86%, respectively) (Scheme 2). The complete reaction was monitored by ¹H NMR experiment using in both cases the shift of CH₂-C=O signal (H₁₇) from 2.88 to 2.34 ppm as well as the appearance of the propargylic signals corresponding to H₁₉ and H₂₁ at 4.65 and 2.45 ppm.

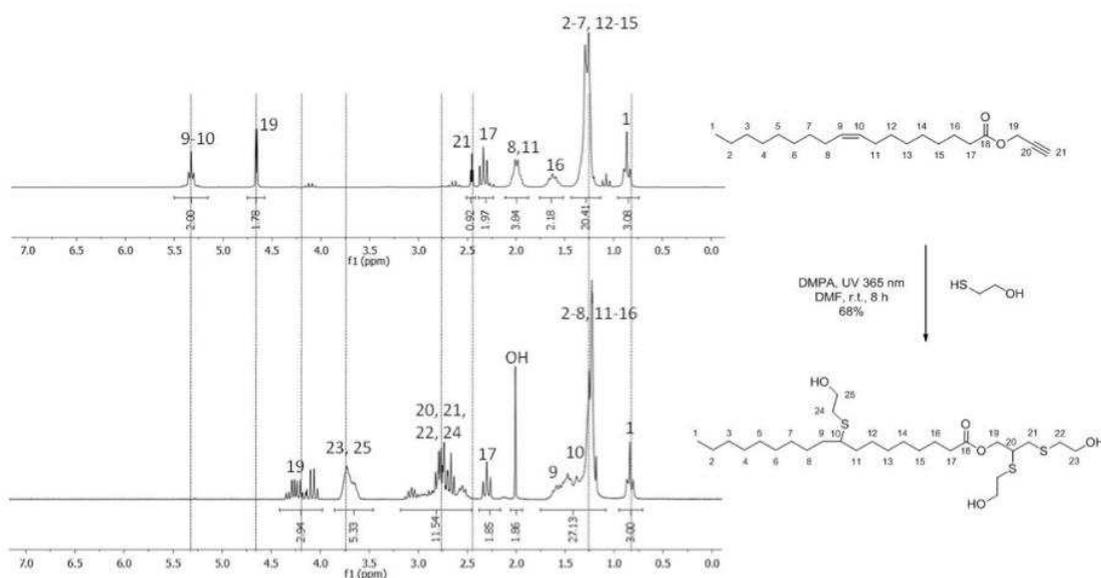


Figure 1

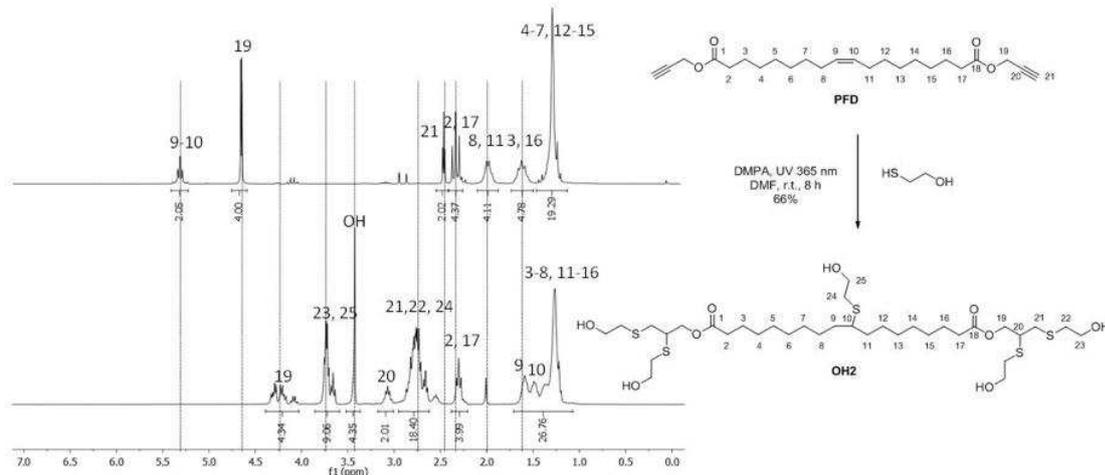


Figure 2

Numerous synthetic methodologies of polyols including ring-opening epoxy group, ozonolysis and hydrosilylation were described in the literature. Unfortunately, in many cases the side reactions accompany the polyol synthesis such as the oligomerization of unsaturated compounds into dimers, trimers, etc. The best way to observe this phenomenon is the utilization of gel permeation chromatography (GPC). By this technique, Curtis *et al.* detected 17% of oligomers during the epoxy ring-opening process by lactic acid followed by

esterification in the case of **2**, described in Table 1.¹⁵ Additionally, Pétrovic *et al.* estimated 18-25% of oligomers for **3** during oxirane ring-opening reaction of epoxidized vegetable oil in presence of methanol.¹⁴ In our case, the formation of oligomers during thiol-unsaturation coupling was detected by GPC using DMAc and polystyrene standards (Figure 3). We noted that the difference between propargylic ester and diester structure is good enough to be detected by this technique and obviously the modification of PFE and PFD by thiol-ene/yne coupling. First, the synthesis of OH1 polyol happened without oligomer formation since no trace was observed at higher retention time and a single GPC trace was detected with a polydispersity index of 1.03. For OH2 polyol, very little oligomers likely dimers appeared as evidenced by the polydispersity index of 1.12. In addition, the shift of the polyol traces related than those of PFD and PFE precursors confirmed the “clicking” of three and five mercaptoethanol units into fatty structures. GPC analysis of OH1 and OH2 show an increase in molecular weight from 400 and 500 g.mol⁻¹ to 1400 and 2400 g.mol⁻¹. The large difference between targeted and experimental molecular weights could be explained by the use of inappropriate polystyrene standards.

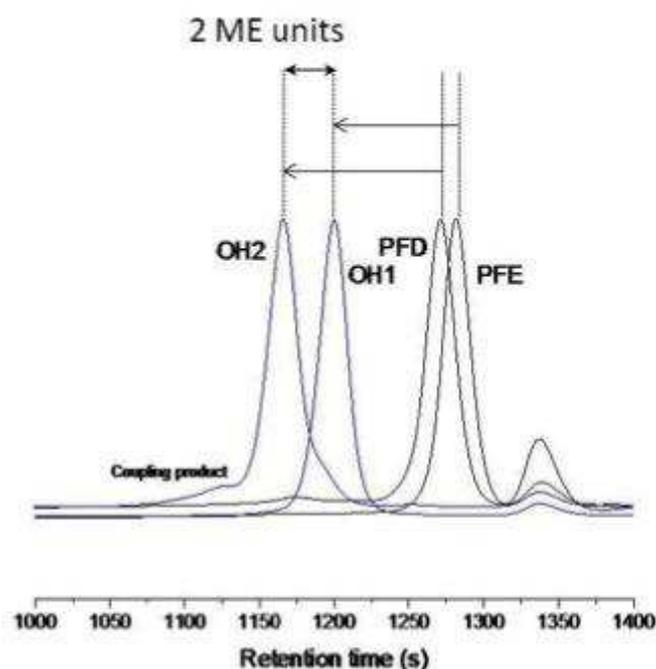


Figure 3

The structure of OH2polyol, alcohol highest functionality of both synthesized, was also explored by LC-ESI/MS technique. As expected, the isomolecular pic $[M+H]^+$ was detected at m/z of 779.40 in accordance with the m/z theoretical value of 779.33. Another pic was observed at m/z of 567.3 and corresponds to $[M-211]^+$, outcome of the breaking of the C-O bond's breaking of one of the two ester group.

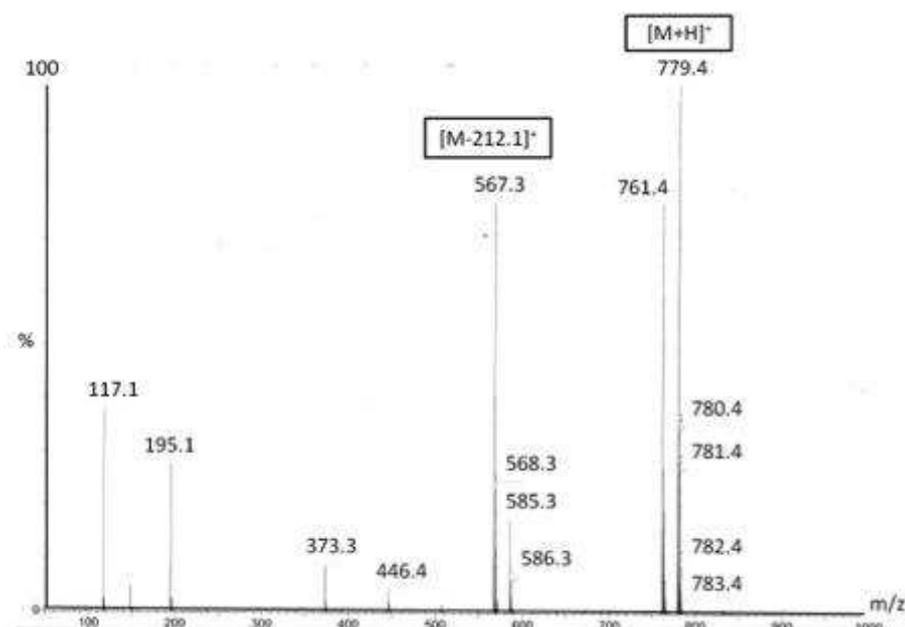
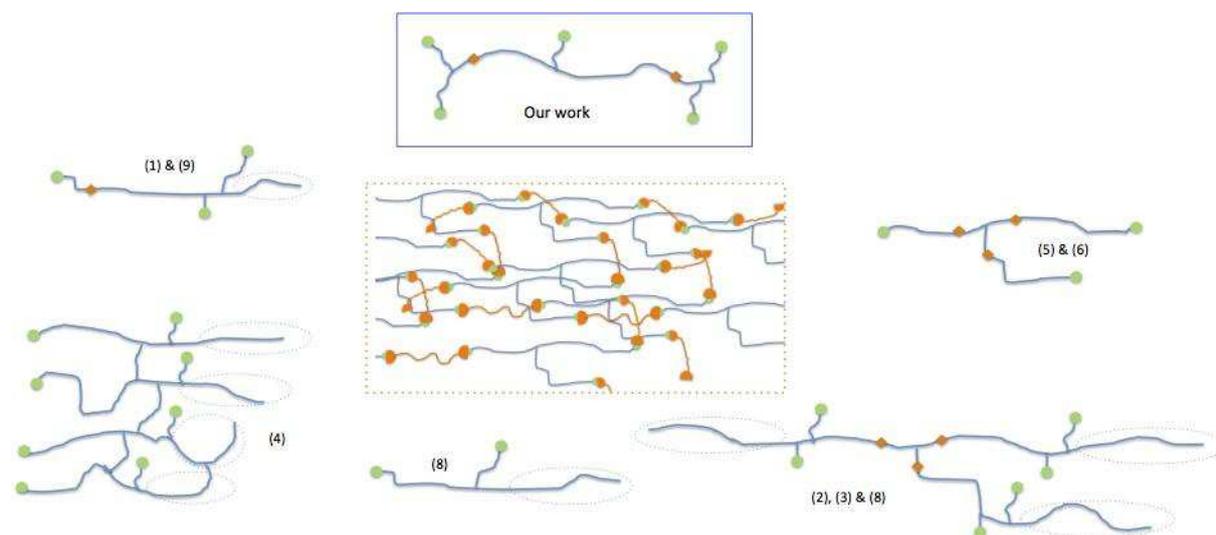


Figure 4

Preparation of PU materials based on lipidic polyols

The polyol structure obviously impacts the density of polyurethane network. Therefore, the T_g values and the thermal properties of the thermosets are influenced by the lipidic polyol structures described in Table 1. It is widespread that the dangling chains of the fatty polyols affect the physical properties of the resulting materials and act as plasticizers decreasing their T_g values.¹⁸ Apart from **5** and **6**, the polyols described in the literature carry one (**1**, **8** and **9**), three (**2**, **3** and **8**) or numerous (**4**) dangling chains as illustrated in Scheme 3. The design of our vegetable oil based polyols considers this aspect. Thus, thanks to fatty acid and diacid

precursors coming from oleic chain, OH1 and OH2 polyols were provided with one or without dangling chain using a simple and versatile thiol-ene/yne coupling approach.



Scheme 3

The comparative study gathers the thermoset polyurethanes coming from MDI and various polyols as compiled in Table 2. The relationship between the polyol structure and the T_g value of the resulting material was discussed. The T_g values were affected by the number of alcohol groups of each fatty chain. This value is directly related to the number of double bonds of precursors fatty chains. Note that the fatty chains are classified according to the number of carbon atoms (n) and of double bonds (m) such as $C_n:m$. For **1**, **3** and **5** polyols, several types of vegetable oils are employed carrying various contents in oleic (C 18:1), linoleic (C 18:2) and linolenic (C 18:3) chains.^{14,15,18} For instance, **3**-based PU using canola oil (iodine index of 114) or linseed oil (iodine index of 182) have got a T_g value of 32 and 77 °C, respectively.¹⁴ In short, as expected, the high level of unsaturations (iodine index closed to 220) favors the high T_g value in relation to the crosslinking density. The T_g values also depend on the strategy of incorporation of alcohol groups on fatty chains (TEC, ring-opening (RO) of

oxirane). For instance, even if in all cases, fatty precursors are vegetable oils (TAG structure), PU based on **2**(RO),**3**(RO)and **7**(TEC) offered a large panel of Tg values ranging from 25 °C for **7** until 96 °C for **2**.^{14,16,20} Thus, the nature of the functional alcohol unit (lactic acid for **2** and methanol for **3**) added on epoxidized vegetable oil influenced the Tg value. Interestingly, the three-arm star structure (**5** and **6**) having a terminal alcohol group exhibited low Tg values ranging from 22 and 39 °C.^{18,19} This result can be explained by the flexibility of the alkyl chain bearing alcohol group and the long distance between two reactive alcohol functions producing a network with wide mesh.

As mentioned above, the presence of dangling chain in polyol structure decreased the Tg value by plasticization of the Tg value. Besides the oligomer nature of **7**, low Tg values were measured (-3 and 57 °C) likely caused by the dangling chain.²⁷ By TEC functionalization, the same problem occurred with modified TAG (**7**) and modified fatty acid (**8**).^{20,21} The Tg values varied between 25 and 56 °C. Surprisingly, the structure **1** exhibited the highest Tg value (114 °C) with 3 alcohol groups (2 secondary and 1 primary) with one dangling chain.¹⁵ In order to enhance the alcohol density in polyol structure without dangling chain, Cadiz *et al.* reported the thiol-yne functionalization of 10-undecynoic and 9-octadecynoic acids after bromination of double bond, deshydrobromination into alkenic bond followed by esterification of acid group.²⁵ The resulting PU thermosets have a Tg value up to 59 °C. In our methodology, even if we kept the TYC approach, a shorter strategy was used to incorporate an alkenyl group in fatty acid (PFE) and diacid (PFD) structures. Unlike Cadiz, thiol-yne coupling led to the introduction of a terminal alkenyl group by esterification instead of bromination/deshydrobromination of an internal double bond.

Table 2. Comparison of polyurethanes synthesized in this work and in the literature.

Reference	[NCO]/[OH]	T _g (°C)	T _{5% loss} (°C)
(1)	1.1 / 1	69 - 114 ^c	---
(2)	1.05 / 1	96 ^b	273 ^e
(3)	1.02 / 1	30 - 77 ^b	---
(4)	1.02 / 1	-3 - 57 ^d	337 - 352
(5)	1.02 / 1	22 & 36	330 & 337 ^e
(6)	1.02 / 1	39	322 ^f
(7)	1.05 / 1	25 ^a	---
(8)	1 / 1	8 - 56	269 - 290
(9)	1 / 1	42 - 59	245
PU1	1 / 1	36	297
	1.1 / 1	45	295
PU2	1 / 1	68	279
	1.1 / 1	72	282

PU materials were curing at 110°C apart from 65 °C (a), 80°C (b) and 100°C (c). ^d: T_g value determined by DMA experiment. ^e: deduced from figure. ^f: temperature of 10% of weight loss.

The thermoset polyurethane materials were prepared by mixing OH1 or OH2 with 4,4'-methylenebis(phenyl isocyanate) (MDI) at 60 °C in aluminum mold. The mixture was cured at 60 °C for 24h and post-cured at 110°C for 24h. The [NCO]/[OH] ratio ranged from 1/1 to 1.1/1 being careful to keep the NCO amount superior than OH amount in order to compensate the consumption of NCO species by side reactions. The polyurethane crosslinking was confirmed by FTIR analysis as illustrated by the overlapping of OH1, MDI and PU1 spectra in Figure 5. The total disappearance of -N=C=O stretching of the isocyanate moiety at 2240 cm⁻¹ in PU1 means that the network was complete. Furthermore, the stretching vibration of C=O urethane appeared at 1708 cm⁻¹ and overlapped with the C=O ester band at 1736 cm⁻¹. The N-H deformation as well as C-N stretching vibration occurred at 1520 and 1215 cm⁻¹, respectively. In addition, the broad band at 3500 cm⁻¹ corresponding to O-H stretching, shifted to lower frequencies at 3350 cm⁻¹, characteristic of N-H stretching.

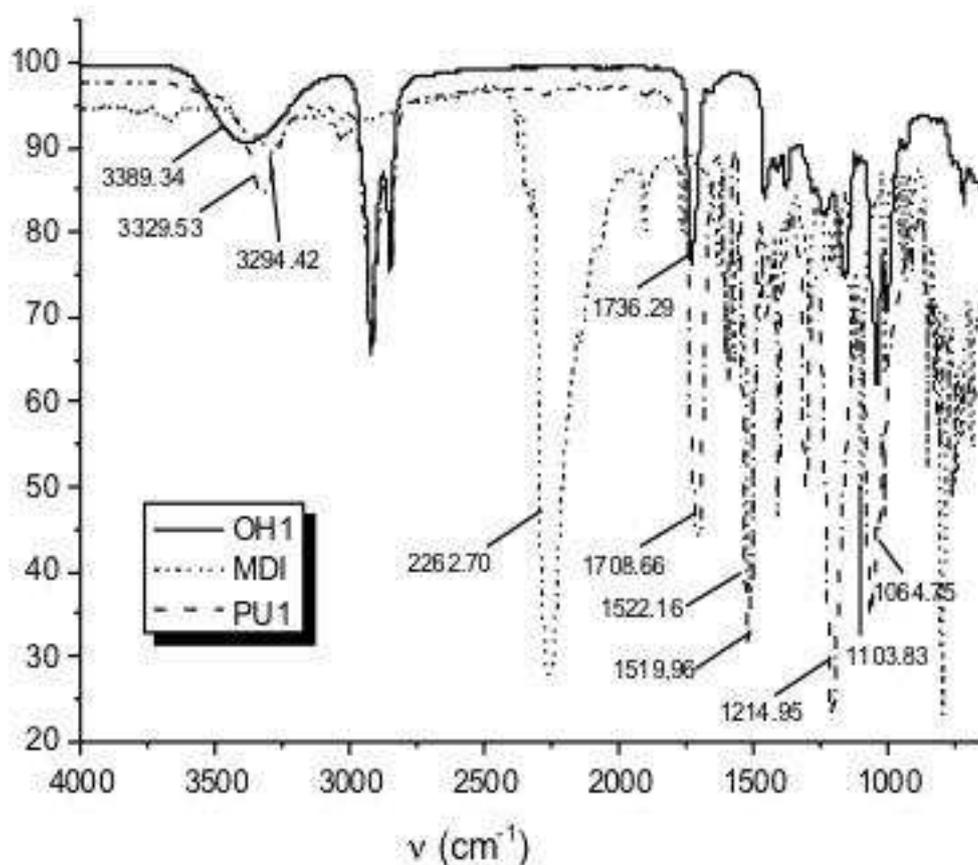


Figure 5

The thermal behaviors of PU1 and PU2 coming from OH1 and OH2 were investigated by DSC technique as shown in Figure 6. First, the glass transition temperatures of lipidic polyols (before crosslinking) were estimated. The T_g of OH1 and OH2 polyols were found to be -70 and -58 °C, respectively (Figure 6, left). The larger number of alcohol groups reduced the mobility of fatty chain and increased the T_g value. Secondly, the same experiments were conducted on resulting thermoset PUs (Figure 6, right). The influence of $[NCO]/[OH]$ ratio on the crosslinking density and the T_g value was also investigated and reported in Table 2. For both polyols, the best results were observed for slight excess in isocyanate: 1.1/1 related than 1/1 as widely described in the literature. It is noteworthy that higher T_g value was measured for PU2 in comparison to PU1 (72 and 45 °C, respectively). This difference could be explained by the presence of dangling chain in the structure of OH1 in opposition to OH2 as well as the

densification of the network resulting in higher functionality in alcohol groups in the latter case.

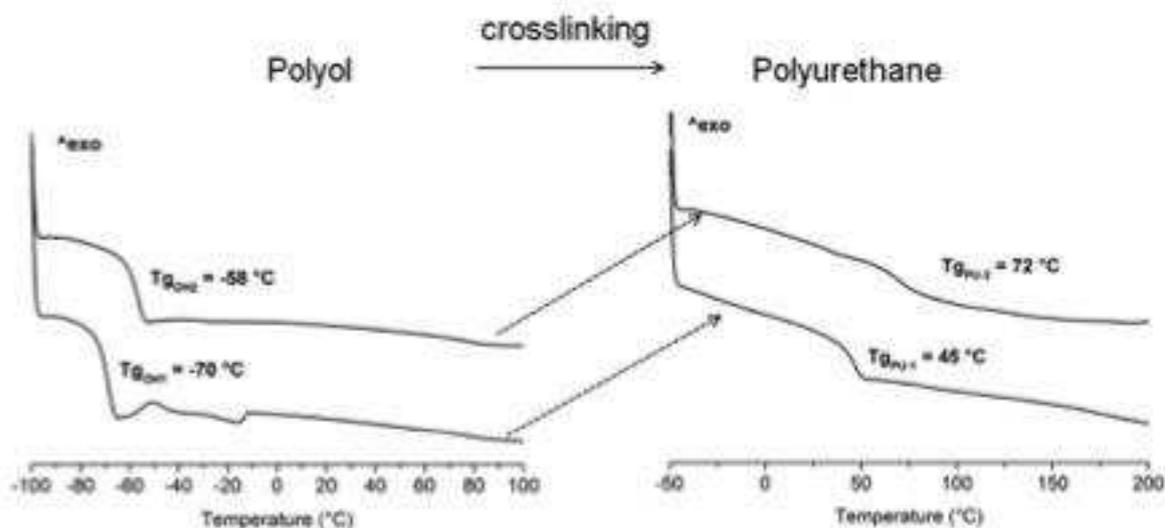


Figure 6

The thermal stability of PU1 and PU2 thermosets was investigated by thermogravimetric analysis (TGA) in nitrogen stream, and the results were collected in Figure 7. As previously reported, the thermal stability of polyurethanes is relatively low. Our results were in accordance with other thermoset PUs coming from lipidic polyols and synthesized by TEC or TYC methodology. At weight loss of 5%, the degradation temperatures of PU1 and PU2 were 295 and 282 °C, respectively whereas those of Cadiz are 269-290 °C for TEC-based polyol (8) and 245 °C for TYC-based polyol (9) (Table 2).^{21,25} Moreover, the well-known thermal degradation of polyurethanes undergoes in a three-step process.²¹ As described, our products degraded in two overlapping steps: i) the first step around 325 °C results in the degradation of weak urethane bonds through the dissociation to isocyanate and alcohol and ii) the second step occurs at 343 °C and corresponds to the decomposition and the char formation of crosslinked polymer networks. Finally, the third decomposition took place at 428-468 °C and corresponds to the gasification of any remaining components.

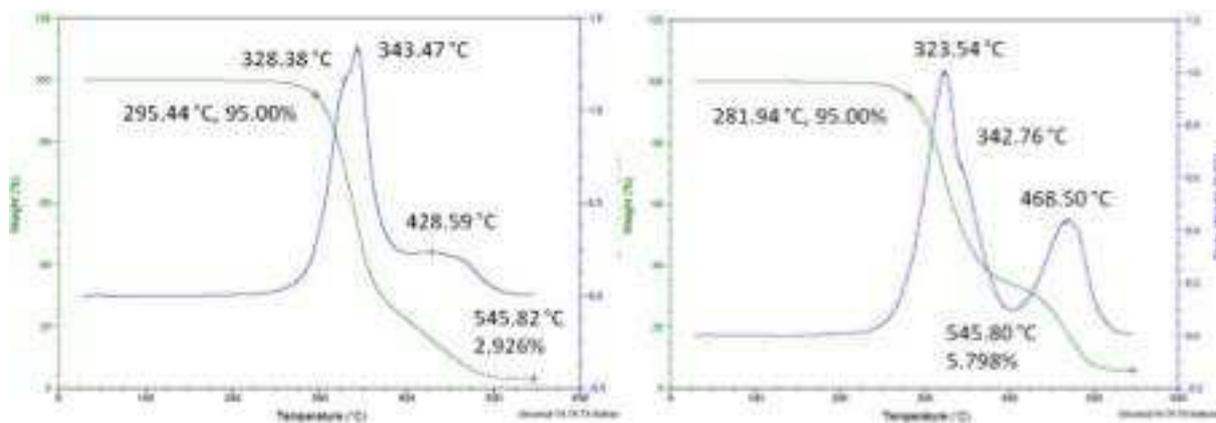


Figure 7

Conclusion

In this contribution, propargylic fatty acid and diacid were synthesized in good yields. We showed that thiol-ene/yne coupling is an effective approach to synthesize lipidic polyols without oligomers. Foroleicdiacid, polyol without dangling chain was prepared and produced polyurethane materials with Tg value of 72°C after optimization of the crosslinking parameters (temperature and [NCO]/[OH]). Comparing our results to those reported in the overview regarding to plant oil-based crosslinked polyurethanes, we showed a typical thermal stability in a three-step process of plant oil-based thermoset polyurethanes. Thus, through the synthesis of these lipidic polyols, we illustrated the opportunity of TYC/TEC functionalization in the synthesis of high functional monomers and branched polymers using bio-based building blocks.

Acknowledgement

The authors gratefully acknowledge S.I.A. for their financial support.

References

- (1) Gandini, A. *Macromolecules***2008**, *41*, 9491.
- (2) Derksen, J. T. P.; Petrus Cuperus, F.; Kolster, P. *Progress in Organic Coatings***1996**, *27*, 45.
- (3) Yu, L.; Dean, K.; Li, L. *Progress in Polymer Science***2006**, *31*, 576.
- (4) Vieira, M. G. A.; da Silva, M. A.; dos Santos, L. O.; Beppu, M. M. *European Polymer Journal***2011**, *47*, 254.
- (5) Alexandridis, P. *Current Opinion in Colloid & Interface Science***1996**, *1*, 490.
- (6) Seniha Güner, F.; Yağcı, Y.; Tuncer Erciyes, A. *Progress in Polymer Science***2006**, *31*, 633.
- (7) Rybak, A.; Meier, M. A. R. *Green Chemistry***2007**, *9*, 1356.
- (8) Kathalewar, M. S.; Joshi, P. B.; Sabnis, A. S.; Malshe, V. C. *RSC Advances***2013**, *3*, 4110.
- (9) Benyahya, S.; Habas, J.-P.; Auvergne, R.; Lapinte, V.; Caillol, S. *Polymer International***2012**, *61*, 1666.
- (10) Stemmelen, M.; Travelet, C.; Lapinte, V.; Borsali, R.; Robin, J.-J. *Polymer Chemistry***2013**, *4*, 1445.
- (11) Gandini, A. In *Epoxy Polymers*; Wiley-VCH Verlag GmbH & Co. KGaA: 2010, p 55.
- (12) Stemmelen, M.; Pessel, F.; Lapinte, V.; Caillol, S.; Habas, J. P.; Robin, J. J. *Journal of Polymer Science Part A: Polymer Chemistry***2011**, *49*, 2434.
- (13) Tan, S. G.; Chow, W. S. *Polymer-Plastics Technology and Engineering***2010**, *49*, 1581.
- (14) Zlatanić, A.; Lava, C.; Zhang, W.; Petrović, Z. S. *Journal of Polymer Science Part B: Polymer Physics***2004**, *42*, 809.
- (15) Kong, X.; Liu, G.; Qi, H.; Curtis, J. M. *Prog. Org. Coat.***2013**, *76*, 1151.
- (16) Miao, S.; Zhang, S.; Su, Z.; Wang, P. *J. Polym. Sci., Part A: Polym. Chem.***2010**, *48*, 243.
- (17) Del Rio, E.; Galià, M.; Cádiz, V.; Lligadas, G.; Ronda, J. C. *Journal of Polymer Science Part A: Polymer Chemistry***2010**, *48*, 4995.
- (18) Petrović, Z. S.; Zhang, W.; Javni, I. *Biomacromolecules***2005**, *6*, 713.
- (19) Lligadas, G.; Ronda, J. C.; Galia, M.; Cadiz, V. *Biomacromolecules***2006**, *7*, 2420.
- (20) Desroches, M.; Caillol, S.; Lapinte, V.; Auvergne, R. m.; Boutevin, B. *Macromolecules***2011**, *44*, 2489.
- (21) González-Paz, R. J.; Lluch, C.; Lligadas, G.; Ronda, J. C.; Galià, M.; Cádiz, V. *Journal of Polymer Science Part A: Polymer Chemistry***2011**, *49*, 2407.
- (22) Türünç, O.; Meier, M. A. R. *Macromolecular Rapid Communications***2010**, *31*, 1822.
- (23) Yao, B.; Sun, J.; Qin, A.; Tang, B. *Chin. Sci. Bull.***2013**, *58*, 2711.
- (24) Fairbanks, B. D.; Scott, T. F.; Kloxin, C. J.; Anseth, K. S.; Bowman, C. N. *Macromolecules***2008**, *42*, 211.
- (25) Gonzalez-Paz, R. J.; Lligadas, G.; Ronda, J. C.; Galia, M.; Cadiz, V. *Polymer Chemistry***2012**, *3*, 2471.
- (26) Lligadas, G. *Macromolecular Chemistry and Physics***2013**, *214*, 415.
- (27) Del, R. E.; Lligadas, G.; Ronda, J. C.; Galia, M.; Cadiz, V. *J. Polym. Sci., Part A: Polym. Chem.***2010**, *48*, 5009.

Table captions

Table 1. Comparison of polyols synthesized in this work and in the literature.

Table 2. Comparison of polyurethanes synthesized in this work and in the literature.

Scheme captions

Scheme 1. General mechanism of thiol-ene and thiol-yne couplings between alkene and alkyne and thiol - Application to PFE and PFD and mercaptoethanol.

Scheme 2. Synthesis of propargylic fatty ester: PFE and PFD.

Scheme 3. Schematic network based on various architectures of lipidic polyols.

Figure captions

Figure 1. ^1H NMR spectra of PFE and OH1 in CDCl_3 .

Figure 2. ^1H NMR spectra of PFD and OH2 in CDCl_3 .

Figure 3. GPC traces in DMAc of PFE and PFD precursors and OH1 and OH2 polyols.

Figure 4. LC ESI/MS spectrum of PFD.

Figure 5. FTIR spectra of OH1, MDI and PU1 (NCO/OH = 1.1).

Figure 6. DSC thermograms of thermoset polyurethanes (right) and the OH1 and OH2 precursors (left).

Figure 7. TGA chromatograms of PU1 (left) and PU2 (right) under nitrogen.

Graphical abstract

Lipidic polyols using Thiol-ene/yne strategy for crosslinked Polyurethanes

Phuoc Dien Pham, Vincent Lapinte,* Yann Raoul, Jean-Jacques Robin

Oleic acid and diacid were converted into lipidic polyols by thiol-ene/yne coupling. They are fully characterized before crosslinked into polyurethane materials. Relatively high-T_g polyurethanes are yielded.

